

An Investigation of Methyl Halide Levels in Lake Sammamish, Sammamish River, and Lake Washington, WA

Lisa Nguyen

Seattle University, Department of Chemistry

Wenlin Huang and Richard Gammon

University of Washington, Department of Chemistry

Introduction

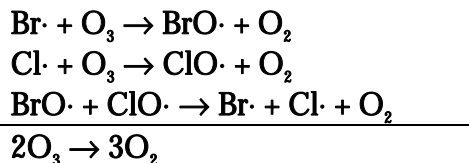
The presence of holes in the ozone (O_3) layer has been highlighted by much media attention in the last few years. While 99% of the atmosphere is composed of N_2 and O_2 , reactive trace gases present in parts per million (ppm) to parts per trillion (ppt) amounts play critical roles in atmospheric gases. There are several classes of trace gases that can cause ozone depletion; the methyl halides are an important source of ozone-depleting radicals. These radicals interrupt the equilibrium between O_2 and O_3 in O_3 formation, and serve to catalyze ozone-depletion.

Methyl chloride is the third-largest source of chlorine (Cl) after the chlorofluorocarbons (CFCs), CFC-12 and CFC-11. Currently, the amount of Cl in the air is estimated at 3800 ppt (Butler and Rodriguez, 1996). The majority of the Cl comes from the CFCs, but methyl chloride (CH_3Cl) does contribute to this amount. The average annual amount of CH_3Cl in clean background air is 620 ppt (Butler and Rodriguez, 1996). Unlike CFC-12, which has an average lifetime of 140 years, CH_3Cl has a short lifetime of 1–2 yr (Butler and Rodriguez, 1996). The principal sources of CH_3Cl are natural: oceanic emissions and fires. CH_3Cl 's main sink is tropospheric oxidation with the hydroxyl radical.

Much more is known about methyl bromide (CH_3Br). CH_3Br is the largest carrier of stratospheric bromide (Br). The average annual amount in background air is 10 ppt, with a 1.3 northern hemisphere (NH)/southern hemisphere (SH) gradient (Butler and Rodriguez, 1996). Uncertainty still exists regarding the lifetime of CH_3Br , but it is short, approximately one year. The main natural source of CH_3Br comes from oceanic emissions from algae and phytoplankton. Biomass burning accounts for another natural source of CH_3Br . The rest of the principal sources of CH_3Br are anthropogenic: agricultural applications, leaded gasoline, combustion, and structural fumigation. Principal sinks of CH_3Br are: atmospheric reaction with $\cdot OH$, $Cl\cdot$, and $NO_3\cdot$; photolysis; dissolution in seawater; and hydrolysis reaction with Cl^- (Butler and Rodriguez, 1996).

Research has focused more intently on CH_3Br than on CH_3Cl because Br cycles more rapidly through the environment than Cl. On an atom-per-atom basis, Br is 50 times more effective than Cl in removing stratospheric ozone. While a smaller amount of Br is present in the stratosphere, 10 ppt of CH_3Br would be equivalent to 500 ppt of Cl, making Br a considerable factor in ozone depletion. In fact, it is estimated that 20–25% of the annual Antarctic ozone hole is caused by Br-catalyzed destruction of ozone, which occurs through the following proposed mechanism (Huang, 1997):

(1)



Unlike the CFCs, which are anthropogenic in origin, CH_3Br is produced both naturally and anthropogenically. An abundant amount of research has been devoted to finding the precise budget for CH_3Br

sources and sinks because the effectiveness of restrictions on man-made CH_3Br sources on ozone depletion must be determined. Currently, the 1992 Copenhagen Amendments to the 1987 Montreal Protocol between industrialized and developing nations states that the production of CH_3Br in industrialized nations has been frozen to 1991 levels; production of CH_3Br will be phased-out of industrialized nations by the year 2000. Developing nations have 10 more years to phase-out CH_3Br production (Butler and Rodriguez, 1996). Fortunately, since CH_3Br has a short lifetime, the effects of these restrictions should cause a notable reduction in stratospheric Br in less than a decade after cessation of anthropogenic emissions. This differs considerably from the long-lived CFCs: even if all CFC emissions were stopped, half of the CFC-12 present today would still reside in the atmosphere in 100 years (Butler and Rodriguez, 1996).

To determine whether restrictions on anthropogenic methyl halide use would significantly impact the Puget Sound region, levels of methyl bromide and methyl chloride were measured in Lake Sammamish, Sammamish River, and Lake Washington in order to ascertain whether any point-sources of methyl halides that were anthropogenic in origin existed.

Materials and Methods

Air samples were pumped into Rasmussen or Krasnik air canisters, using a battery-powered diaphragm pump. Water samples were obtained in 100-mL glass syringes. All samples were taken several inches below the surface. Lake Sammamish samples were taken at least 20 meters away from the shore; Sammamish River samples were taken 1–3 m away from the shore; Lake Washington samples at Log Boom County Park and Juanita Beach County Park were taken approximately 100 m from the shore.

An extraction board that utilized cryotrapping was used to concentrate sample gases. The trap used to concentrate the methyl halides was packed with 5 cm of glass wool, followed by 5 cm of Porasil C (80/100 mesh), 5 cm of Porapak T (80/100 mesh) and 5 cm of glass wool. Air samples were injected into the board and were concentrated in the trap for 4 minutes at -40°C by immersion into a Dewar flask containing ethanol cooled with dry ice. After concentration, the trap was heated to 100°C by immersion into a Dewar flask of boiling water, and the sample gases were injected into the HP 5890 Series 2 Gas Chromatography Instrument (Hewlett-Packard). Water samples were stripped of methyl halides by the N_2 carrier gas for eight minutes in the stripping chamber. The stripped samples proceeded into the trap as outlined above.

Sample components were separated by a 30-m x 0.52-mm DB-624 capillary pre-column followed by a 75-m x 0.52-mm DB-624 capillary main column (J & W Scientific Products). The pre-column allowed for backflushing of trap contents after the compounds of interest entered the main column. Eluting components were detected using an HP G1223A ECD (Hewlett-Packard). Chrom Perfect Direct[®] software was used to perform peak integration. Data was reduced using calculations described by Bullister and Weiss (Bullister and Weiss, 1988).

Results

Tables 1 and 2 show air measurement data. All air samples taken showed normal background levels for methyl bromide and methyl chloride. The average background level of CH_3Br is 10–12 ppt, while the average background level of CH_3Cl is 620 ppt.

Table 1. CH_3Br and CH_3Cl air measurements (7/31/97).

Location	CH_3Br (ppt)	CH_3Cl (ppt)
Log Boom County Park	11.0 ± 0.4	528 ± 21
Sammamish R. Turf Farm	11.4 ± 0.5	539 ± 22
Idylwood Park	11.9 ± 0.5	535 ± 21

Table 2. Summer and winter CH₃Br air measurements (9/2/97, 2/26/98).

Location	CH ₃ Br (ppt) 9/2/97	CH ₃ Br (ppt) 2/26/98
Log Boom County Park	9.0 ±0.4	11.0 ±0.4
Juanita Beach County Park	9.5 ±0.4	10.8 ±0.4

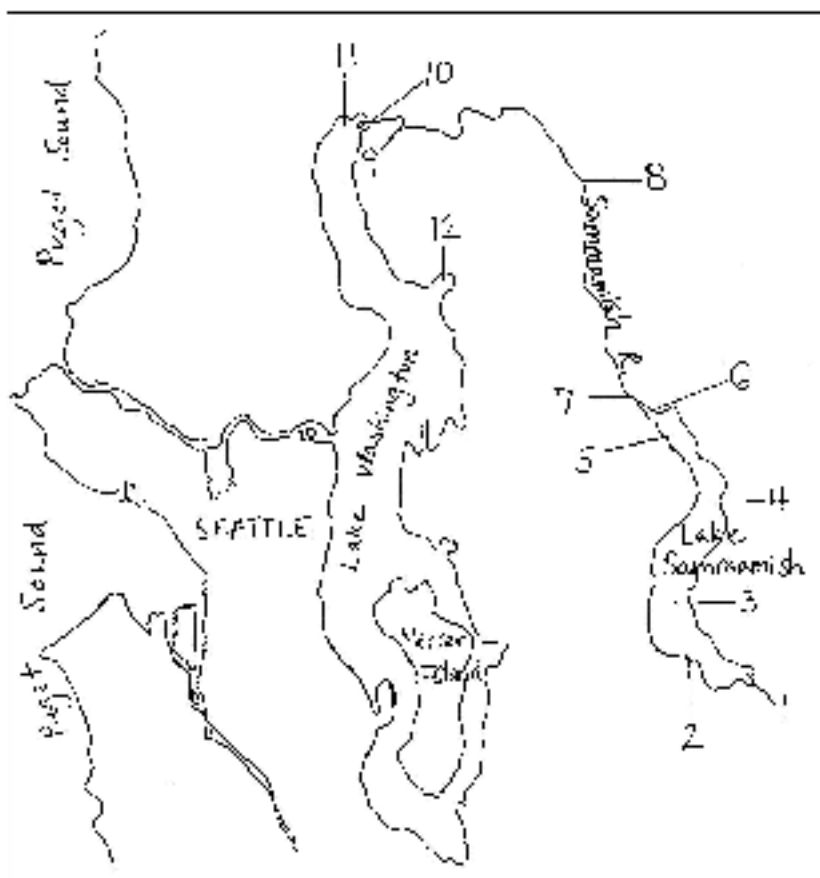


Figure 1. Sample site locations.

- | | |
|--------------------------------|--|
| 1) L. Sammamish/Issaquah Creek | 7) Sammamish R./Marymoor Co. Park |
| 2) L. Sammamish/Lewis Creek | 8) Sammamish R./Turf Farms |
| 3) L. Sammamish | 9) Sammamish R./Swamp Creek |
| 4) L. Sammamish | 10) Sammamish R./Kenmore Boat Launch |
| 5) L. Sammamish/Idylwood Park | 11) L. Washington/Log Boom Co. Park |
| 6) L. Sammamish/Sammamish R. | 12) L. Washington/Juanita Beach Co. Park |

Water samples of methyl bromide and methyl chloride were taken during the summer from Lake Sammamish, Sammamish River, and the north end of Lake Washington. Figure 1 shows a map of the locations where samples were obtained. Figure 2 shows the surface concentration of the methyl halide samples taken in the summer.

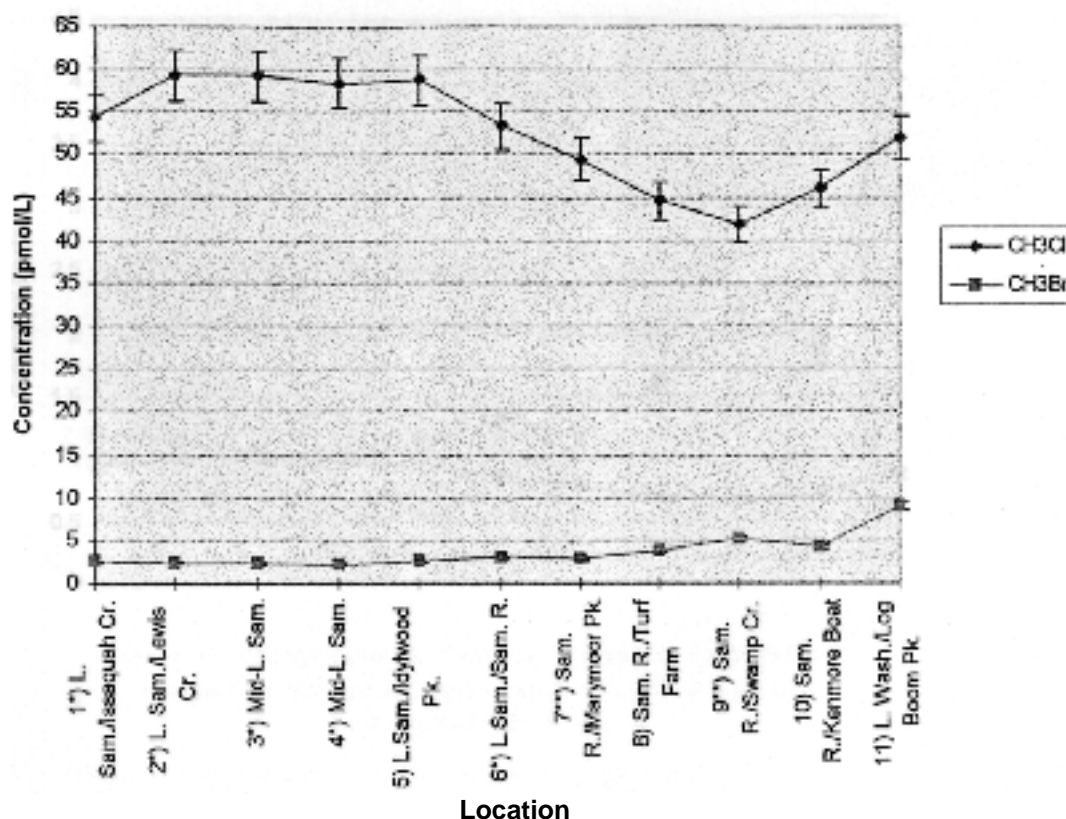


Figure 2. Methyl bromide and methyl chloride surface concentrations in Lake Sammamish, Sammamish River, and Lake Washington (7/31/97, 8/6/97*, 8/11/97**).

As shown from Figure 2, methyl bromide concentrations were low in Lake Sammamish and rose traveling along Sammamish River and the north end of Lake Washington. The concentration obtained at Log Boom County Park, $\text{CH}_3\text{Br} = 9.06 \pm 0.45$ pmol/L was quite high, approximately 3 times higher than the values obtained in Lake Sammamish. A value obtained from Madison Park, in the middle of Lake Washington, on 7/15/97 showed a CH_3Br concentration of 3.47 ± 0.17 pmol/L, which was less than half the concentration of the value obtained at Log Boom County Park. Thus, further measurements comparing the CH_3Br values from Log Boom County Park and the similar, non-industrialized Juanita Beach County Park, were conducted to determine whether the high value obtained at Log Boom County Park was anthropogenic in origin.

The methyl chloride concentrations were highest in Lake Sammamish, approximately 60 pmol/L, and then decreased along the Sammamish River. The CH_3Cl concentration rose again at the end of the Sammamish River and the north end of Lake Washington, although the values did not rise to the same levels as were present in Lake Sammamish.

Figure 3 shows the summer-time saturation factors of CH_3Br and CH_3Cl seen at the sites. The trends follow those seen in Figure 2. All of the methyl bromide values show that the water was over 100% saturated. Very high levels of CH_3Br saturation were seen towards the end of Sammamish River and the north end of Lake Washington, with the saturation at Log Boom County Park greater than 400%. The methyl chloride saturation factor values seen in Lake Sammamish were approximately at equilibrium, and decreased below equilibrium in Sammamish River and the north end of Lake Washington.

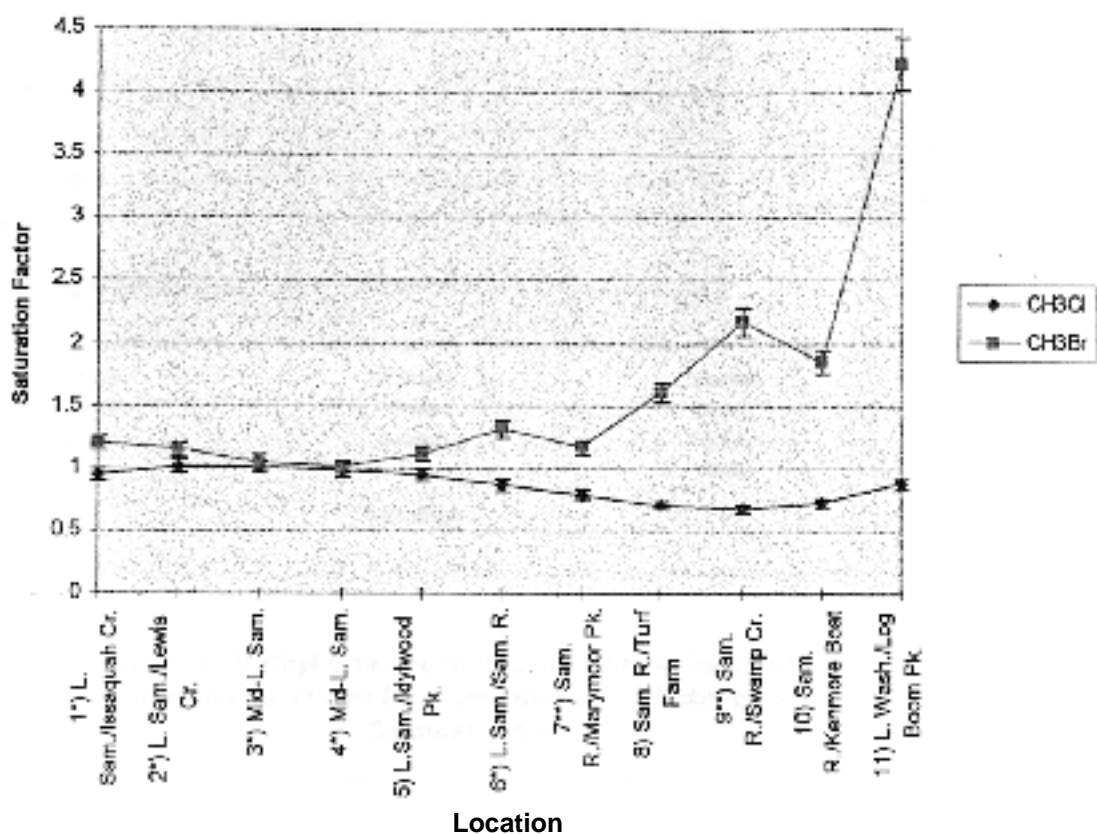


Figure 3. Methyl bromide and Methyl chloride surface saturation factors for Lake Sammamish, Sammamish River, and Lake Washington (7/31/97, 8/6/97*, 8/11/97**).

Figures 4 and 5 show the results for methyl bromide measurements taken at Log Boom County Park, Kenmore Boat Launch (at the end of Sammamish River), and Juanita Beach County Park. The measurements were conducted in summer and winter to determine whether the high sources of methyl bromide were anthropogenic or natural in origin.

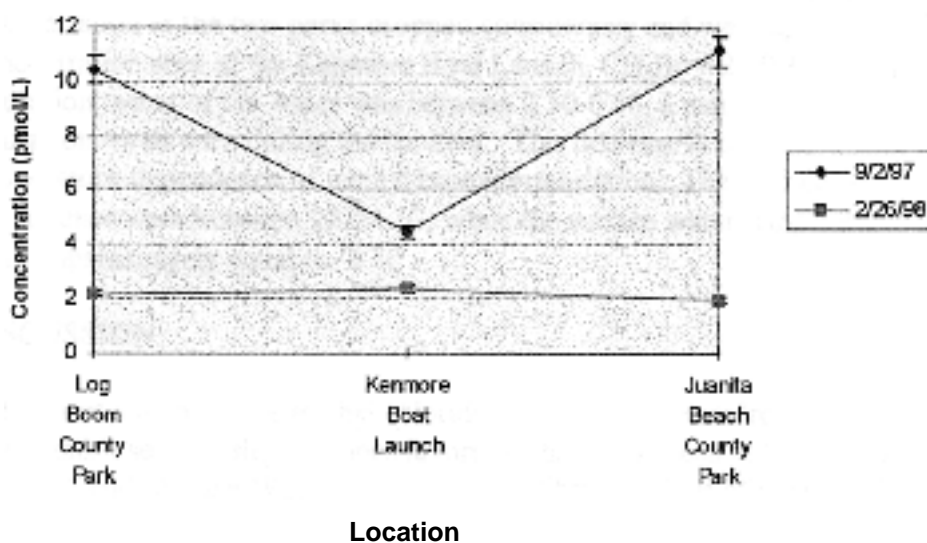


Figure 4. Washington and Sammamish River methyl bromide surface water concentration, summer vs. winter.

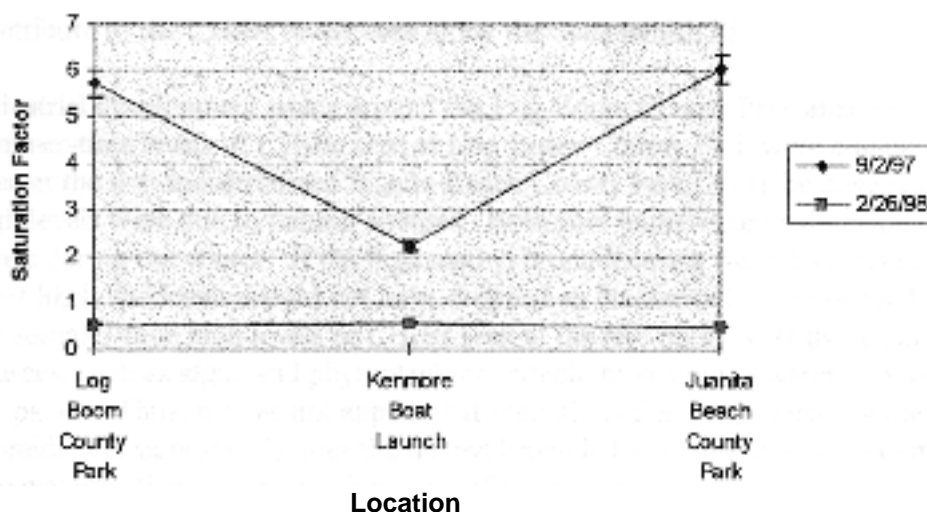


Figure 5. Methyl bromide surface saturation factors for summer vs. winter measures of Lake Washington and Sammamish River.

Figure 4 shows that in the summer-time, both Log Boom County Park and Juanita Beach County Park had comparable levels of methyl bromide, with CH_3Br concentrations at 10.4 ± 0.5 pmol/L and 11.2 ± 0.6 pmol/L, respectively. Figure 5 shows that both locations were highly saturated, over 500%. Interestingly, the summer-time CH_3Br concentration and saturation factor seen at the end of Sammamish River (near Kenmore Boat Launch) were less than half the values obtained at the two parks on Lake Washington, even though Kenmore Boat Launch is less than one mile away from Log Boom County Park.

The winter-time CH_3Br values at the same locations showed that the methyl bromide concentration at the two parks dropped considerably and were approximately equal to the concentration seen at the Kenmore Boat Launch, $\text{CH}_3\text{Br} = 2.39 \pm 0.1$ pmol/L. The saturation factor of the water was between 0.50–0.58, a marked decrease from the saturation levels seen during the summer. This decrease is consistent with the temperature-dependence of methyl bromide saturation. The surface water temperatures in the summer were between 22–24° C, while the surface water temperatures in the winter were approximately equal to 7° C.

Discussion

In terms of summer-time methyl chloride production, the environmental conditions in Lake Sammamish seemed slightly more favorable than those seen in the Sammamish River or in the north end of Lake Washington. The equilibrium values of the CH_3Cl saturation factors and the air measurements showing normal background levels of CH_3Cl , indicated that there were no unusually large point-sources of CH_3Cl .

The levels of CH_3Br seen along the Sammamish River, especially those near the turf farms, did not show unusually large values. If the turf farms used methyl bromide as a fumigant, it may be that the samples were not taken immediately after fumigation. Nevertheless, from the values obtained, it appeared that anthropogenic sources did not significantly contribute to the CH_3Br levels seen along the Sammamish River.

Industrial development exists around the Log Boom County Park area; however, since the summer-time levels of CH_3Br seen at Log Boom County Park were comparable to those seen at the non-industrialized Juanita Beach County Park, it can be concluded that the high levels were due to natural sources. Both sites experienced a dramatic drop in CH_3Br levels during the winter. If the high methyl bromide levels were from man-made activity, most likely the levels would not have dropped so dramatically. These results confirm that the summer-time high levels of CH_3Br seen at the two parks

were likely due to natural sources, such as algae and phytoplankton, which thrived in the warm, shallow waters of the parks. Thus, it does not appear that reduction of anthropogenic sources of methyl bromide will significantly alter the methyl bromide levels seen in Lake Sammamish, Sammamish River, or the northern end of Lake Washington.

Acknowledgments

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